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1. Your reference	JR/P9210GB
2. Patent application number *(The Patent Office will fill in this part)*	0304276.9
3. Full name, address and postcode of the or of each applicant *(underline all surnames)*	DOW BENELUX BV P O Box 48 4530 AA Terneuzen The Netherlands
Patents ADP number *(if you know it)*	4329769001
If the applicant is a corporate body, give the country/state of its incorporation	The Netherlands
4. Title of the invention	REACTIVE HOT MELT ADHESIVE
5. Name of your agent *(if you have one)*	W. H. Beck, Greener & Co.
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	W. H. Beck, Greener & Co. 7 Stone Buildings Lincoln's Inn London WC2A 3SZ
Patents ADP number *(if you know it)*	323001 ✓

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Continuation sheets of this form	
Description	22
Claim *(s)*	4 DLA
Abstract	1
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Request for preliminary examination and search *(Patents Form 9/77)*	
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11. I/We request the grant of a patent on the basis of this application.

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12. Name and daytime telephone number of person to contact in the United Kingdom: Mr. J. Raynor - (020) 7405 0921

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Reactive Hot Melt Adhesive

This invention relates to adhesive compositions, and in particular to compositions of the type able to form an initial bond between the parts to be bonded such that the parts can be handled after the initial bonding process, and which subsequently form a permanent bond by a reactive curing process. Such adhesives are generally known as reactive hot melt adhesives (RHMAs). In the automotive industry, RHMAs may find application, for example as so called "anti-flutter" adhesives, (i.e. to fill the space between the reinforcing structure of a vehicle part and the outer skin panels in order to lessen vibration), and as "sealer" adhesives for use in an automotive body shop or paint-shop (for example to protect weld-points or flange/gaps from corrosive attacks and humidity, water, dust particles intrusion).

They may also be used for other applications, for example to bond two metal or plastics substrates and/or to increase damping or stiffening.

Currently, these functions are fulfilled by compositions with paste-like consistency, with a range of viscosity depending on the application. Generally, existing reactive compositions are based on rubber, PVC, or acrylics.

For use in body-shops in the automotive industry, where parts can be oily, these compositions need to have enough viscosity/strength after application in order to withstand the panel degreasing and pre-treatment process (so called wash-off resistance to dipping and jet-spray of water/alkaline/dispersion solutions). This requirement for high viscosity limits the rate at which material can be supplied pumped to the application nozzle. Generally the tube length to the nozzle cannot exceed 10 to 15 meters.

Since a single adhesive may be needed to be applied at several locations spread over hundreds of meters in an automotive plant, a specific dispensing system (pump and associated room area, equipment, drum storage and logistics) need to be installed for each location.

Furthermore, even this high viscosity level is often not sufficient to guarantee resistance to wash-off in critical areas of the body, does not give enough green strength, and can not prevent de-localisation of the adhesive during the body-shop process if the part is compressed.

A post-application curing to eliminate the above mentioned issues would affect the cycle time, space requirement, and quality of the parts produced.

It would be desirable to provide materials which do not have the handling difficulties of viscous liquid compositions, but give good wash-off and squeeze resistance, for example by providing a hot melt adhesive in the form of pellets.

Non-reactive hot melt adhesives (so-called "HMA"s) could be used for such applications. HMAs do not have a reactive curing step and accordingly will deform and lose adhesion when heated above their melting point after application. HMAs in general use are commonly based on EVA.

US-A-3,980,735 discloses a HMA comprising an ethylene-vinyl acetate (EVA) copolymer, an unsaturated alkyd resin and an organic peroxide which, according to the description in the patent, can be formulated into pellets and powders. The adhesive composition is not a reactive one however, because the peroxide is substantially fully reacted with the EVA copolymer during the formulation of the adhesive.

WO-A-0172922 discloses thermoplastic polymer particle batches which are only homogenised immediately before use. They are applied immediately after they are homogenised, because after homogenisation, the reaction is initiated and the batches only have a limited pot life.

WO-A-02090454 discloses granulated adhesive based on polyols and isocyanates which are mixed while excluding moisture. Both WO-A-01712922 and WO-A-02090454 rely on moisture as a curing mechanism which limits their pot life.

RHMAs have been available since the 1980s. Because they are capable of curing to a thermosetting material, RHMAs eliminate or reduce many of the problems associated with conventional HMAs, such as poor heat resistance, and water or solvent permeation. The most common RHMAs are based on polyurethanes and are cured using water. There are also several other types of RHMA which are based on non-polyurethane moisture curable polymers or on polymers which are cured by reactive UV curing processes.

Other types of RHMA have also been introduced, which are cured by the use of a free radical initiator such as a peroxide. RHMAs of this type comprising ethylene-vinyl acetate (EVA) copolymers are now in use in the automotive industry. They are supplied in the form of a viscous fluid composition or a pasty composition which can be pumped into a dispensing gun for application. Examples of this type of RHMA include BETAGUARD™ supplied by DOW AUTOMOTIVE. Such compositions often require the use of zinc acrylates as an adhesion promoter for metal which is undesirable because of Environmental, and Health and Safety concerns.

Radical-initiated RHMAs generally have improved dimensional stability and strength and less tendency to sag, as well as better adhesion and corrosion resistance when heated to temperatures above their application temperature, as compared with other types of hot melt adhesive. One difficulty with viscous fluid compositions of this kind however is that the systems which are used for their dispensation and application are sensitive to the rheological properties of the compositions, which in turn depend on the temperature settings of the application equipment. The application equipment must therefore be set up differently for compositions with different rheological properties . This makes it difficult to deal with changes of formulation. In addition, viscous liquid RHMAs must be stored in small drums and processed with pumps through tubes and hoses for use. This produces large amounts of waste and high recycling costs.

It would be desirable to provide RHMA materials which do not have the handling difficulties of viscous liquid compositions, for example, by providing the RHMA in the form of pellets.

In practice, however, pellets produced from RHMA compositions tend to be tacky and/or to have insufficient adhesion during initial application, particularly when applied to metal sheets under oily conditions, such as are typically encountered on a vehicle assembly line.

We have now discovered that a reactive hot melt composition can be prepared which has excellent adhesion and curing properties, and can be formulated into free-flowing pellets or beads, by using an ethylene-acrylic acid copolymer, an ethylene-methacrylic acid copolymer, and/or an ethylene-acrylic acid-methacrylic acid terpolymer as a component of the composition.

According to a first aspect of the invention, there is provided a reactive hot melt composition in the form of free-flowing pellets, the composition comprising:
a cross-linkable resin including at least one copolymer of ethylene with an ethylenically unsaturated monomer, the resin including one or more of an ethylene-acrylic acid copolymer, an ethylene-methacrylic acid copolymer, and an ethylene-acrylic acid-methacrylic acid terpolymer; and
a free radical cross-linking initiator having a 1 hour half-life temperature of from 110 to 170°C.

The said resin preferably constitutes from 37 to 60 % based on the total weight of the composition, and the composition may preferably also comprise from 10 to 30 % based on the total weight of the composition, of an adhesion promoter for providing adhesive properties to the composition at temperatures of from 50 to 100°C, wherein the adhesion promoter comprises at least one of a plasticiser and a tackifier.
The composition also preferably comprises from 10 to 40 % based on the total weight of the composition, of a filler.

According to a preferred aspect of the invention, there is provided a reactive hot melt composition in the form of free-flowing pellets, the composition comprising:
a) from 37 to 60 % based on the total weight of the composition of a cross-linkable resin including at least one copolymer of ethylene with an ethylenically unsaturated monomer;

b) from 10 to 30 % based on the total weight of the composition of an adhesion promoter for providing adhesive properties to the composition at temperatures of from 50 to 100°C, wherein the adhesion promoter comprises at least one of a plasticiser and a tackifier;

c) from 0.5 to 3 % based on the total weight of the composition of a free radical cross-linking initiator having a 1 hour half-life temperature of from 110 to 170°C; and

d) from 10 to 40 % based on the total weight of the composition of a filler;

wherein component a) includes one or more of an ethylene-acrylic acid copolymer, an ethylene-methacrylic acid copolymer, and an ethylene-acrylic acid-methacrylic acid terpolymer.

Compositions of the above type, comprising ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, and/or ethylene-acrylic acid-methacrylic acid terpolymers have been found to have good initial adhesion properties to steel, particularly oily steel, whilst being capable of formulation into pellets which can be conveniently handled. They can be easily melted and applied, using conventional extrusion apparatus.

The compositions of the present invention are useful as RHMAs, in particular as adhesives for oily steel parts in car assembly plants, and have the advantage that as they are in the form of pellets, they may be shipped and stored in a more convenient manner than conventional liquid or pasty resins.

The composition comprises a cross-linkable resin including at least one copolymer of ethylene with an ethylenically unsaturated monomer (component a), wherein the cross-linkable resin includes an ethylene-acrylic acid (EAA) copolymer, an ethylene methacrylic acid (EMAA) copolymer, and/or an ethylene-acrylic acid-methacrylic acid terpolymer (EAAMAA). The cross-linkable resin is used in a total amount of from 37 to 60 %, preferably from 40 to 50 %, by weight, based on the total composition.

The EAA copolymer, EMAA copolymer and/or EAAMAA terpolymer is preferably used in an amount of from 10 % to 40%, more preferably from 15 % to 35 %, most preferably from 15 % to 30 %, by weight, based on the total composition.

The ethylene-acrylic acid copolymer preferably contains from 10 to 30 %, preferably 19 to 25% acrylic acid. Preferably the EAA has a melt flow rate (MFR), when measured according to ISO1133, of more than 100 g/10 min. at 190°C and 2.16 kg. More preferably the EAA has a MFR of from 300 to 1300g/10 min. at 190°C and 2.16 kg. Examples of suitable commercially available ethylene-acrylic acid or ethylene-methacrylic acid copolymers are Primacor™ 5980 and 5990 from The Dow Chemical Company, Nucrel™ from Dupont and Escor™ from Exxon Mobil Chemical. Particularly preferred is Primacor™ 5990.

The ethylene-methacrylic acid copolymer preferably contains from 10 to 30 %, preferably 19 to 25% methacrylic acid. The EMAA preferably has a MFR, when measured according to ISO1133, of from 300 to 1300g/10min. at 190°C and 2.16 kg. An example of a suitable commercially available ethylene-methacrylic acid copolymer is Nucrel™ 2940 from Dupont.

The cross-linkable resin preferably also comprises one or more additional copolymers of ethylene with an ethylenically unsaturated monomer. Suitable additional copolymers include, for example, one or more of ethylene-vinyl acetate copolymers, ethylene-methyl acetate copolymers, ethylene-methylacrylic ester copolymers, ethylene-ethylacrylic ester copolymers, ethylene-butylacrylic ester copolymers. Such polymers when used may be utilised in an amount of up to 25% by weight based on the total composition. Commercially available examples of suitable copolymers include Lotryl™ from Atofina, Enable™ and Optema™ from Exxon Mobil Chemical and Ethyl Acrylate 6182, Ethyl Acrylate 6169, and Ethyl Acrylate 9169 from The Dow Chemical Company. The most preferred additional copolymer is ethylene-vinyl acetate.

The ethylene-vinyl acetate (EVA) copolymer is preferably used in an amount of from 0 to 25 %, more preferably from 5 to 20 % , most preferably from 7 to 18 % by

weight based on the total composition. The EVA copolymer preferably has a vinyl acetate content of greater than 30 %, preferably from 30 to 40 %. The EVA copolymer preferably has a MFR when measured according to ISO 1133 of greater than 50 g/10min., more preferably from 200 to 600 g/min. at 190°C and 2.16kg. Suitable commercially available EVA copolymers include Evatane™ from Atofina and Escorene™ from Exxon Mobil. Particularly preferred are Escorene™ UL05540 (MFR of 60g/10 min.) and Evatane™ 33400 (MFR of 350 to 450 g/10 min. and a vinyl acetate content of 30%).

The cross-linkable resin preferably also comprises one or more additional terpolymers of ethylene with two ethylenically unsaturated monomers. Suitable additional terpolymers are ethylene-vinyl acetate-maleic anhydride polymers (for example Orevac T™), ethylene-acrylate-maleic anhydride polymers (for example Lotader™ AX4720), ethylene-acrylate-glycidyl methacrylate polymers (for example Lotader™ AX8900) and terpolymers containing acrylate and/or methacrylate units and/or methyl acrylate units (for example Escor™ terpolymer from Exxon Mobil Chemical).

The methacrylate- and/or acrylate-ester containing copolymers or terpolymers may be used in an amount of from 0 to 30 %, preferably from 4 to 14 %, more preferably from 5 to 13 % by weight based on the total composition. Such polymers serve to increase the viscosity at low shear rates, and so increase polymer bead stability on application at 100 to 120°C. Methacrylate and/or acrylate-containing polymers, for example an ethylene-acrylic ester-glycidyl methacrylate polymer, preferably contain at least 25% by weight of ethylenically unsaturated monomer units and have an MFR when measured according to ISO 1133 of less than 10 g/10min. at 190°C and 2.16kg. Suitable commercial polymers include Lotader™ AX 8900 which has a MFR of 6 g/10 min. and 32% by weight of ethylenically unsaturated monomer units and AX4720 which has a MFR of 7 g/10 min. and 30 % by weight of ethylenically unsaturated monomer units.

The cross-linkable resin may optionally comprise maleic anhydride grafted elastomers. Suitable commercial examples of maleic anhydride grafted elastomers include Lotader™ 8200, Lotryl™ 35BA 320, Lotryl™ 28BA 175 and Orevac™ terpolymer EVA 9305 from Ato, Exxelor™ VA 1801 (Semi-crystalline) and Exxelor™ VA 1803 (Amorphous) from Exxon, FUSABOND™ N SERIES: MF416D, MN493D, MN494D and MO525D and FUSABOND™ C SERIES MC190D, and MC250D from Dupont. The maleic anhydride grafted elastomer may comprise from 0-20%, preferably from 10-20% of the total composition .

The cross-linkable resin preferably also comprises a rubber, for example a butadiene homopolymer or a copolymer of butadiene with one or more additional monomers such as divinyl benzene or styrene. Such rubbers are also able to provide additional unsaturation and thereby increase the amount of cross-linking. Rubbers may be employed in an amount of from 0 % to 30 %, preferably from 0 % to 20 %, more preferably from 4 % to 10 %, by weight, based on the total composition. Prefered butadiene rubbers are Ameripol ™4503, and Kraton™ D1161, D4123 and D1184.

The adhesion promoter (component (b)) is a material which provides the necessary adhesive properties to the composition before it is cured, i.e. generally at temperatures of up to 110°C. The adhesion promoter comprises at least one of a tackifier and a plasticiser. The adhesion promoter is generally used in an amount from 10 % to 30 %, preferably from 15 % to 25 % by weight based on total composition.

The tackifier is a material capable of imparting tackiness to the composition so that it adheres to the surface to which it is applied, at temperatures of up to 110°C. Suitable tackifiers are well known in the adhesives industry, and are typically hydrocarbon resins, preferably polymers of cycloaliphatic and alkylaromatic monomers. Particularly preferred are so-called cycloaliphatic resins for example NECIRES LF 220/100™ or ESCOREZ 2101™. The tackifier is usually used in an amount of from 0 % to 30 %, preferably from 7 % to 21 %, more preferably from 10 % to 18 %, by weight, based on the total composition.

The second optional component of the adhesion promoter is a plasticiser. Generally, the plasticiser is used in conjunction with a tackifier, but for some resin combinations, sufficient low-temperature adhesion may be achieved by the use of a plasticiser alone. The plasticiser may used in an amount of from 0 % to 10 %, preferably from 2 % to 7 %, more preferably from 3 % to 6 %, by weight, based on the total composition. The purpose of the plasticiser is to control the flexibility of the composition, to improve pre-cure adhesion, and to improve the flow properties and wetting of the composition during application.

Any known type of plasticiser suitable for use with ethylene-acrylic acid-type polymers may be employed, for example phthalates, in particular alkyl phthalates, for example di-isodecylphthalate (DIDP). Other examples of plasticisers which are suitable are diisoheptyl phthalate, diisononyl phthalate, diisodecyl phthalate, diisoundecyl phthalate, diisotridecylphthalate, and diisononyl adipate and diisodecyl adipate. These plasticisers are sold under the tradename Jayflex™ from Exxon Mobil. The most preferred plasticiser is Jayflex™ diisodecyl phthalate. Other suitable plasticisers and oils will be known to one of skill in the art.

The free radical cross-linking initiator (component (c)) is used preferably in an amount of from 0.5 % to 3 %, more preferably from 0.5 % to 2 %, most preferably from 0.5 % to 1.5 %, by weight, based on the total composition. It functions as a curing agent to cross-link the polymer, by acting as a free radical initiator which promotes cross-linking of the polymer chains. The cross-linking initiator is one which has a 1 hour half-life temperature of from 110°C to 170°C. The 1 hour half-life temperature is the temperature at which the half life of the initiator (i.e., the time for half of the initiator molecules to decompose) is one hour. Preferably, the cross-linking agent is a peroxide. Examples of suitable peroxides are:

Peroxide	Trade Name	Temperature for half-life time of (°C) 0.1h	1h
2,5 dimethyl-2,5di(tert-butylperoxy)hexyne-3	Trigonox 145™	182	157
di-tert-butyl peroxide	Trigonox B™	176	154
2,5 dimethyl-2,5-di(tert-butylperoxy)hexane	Trigonox 101™	171	147
tert-butylcumyl peroxide	Trigonox T™	169	146
di(tert-butylperoxyisopropyl)benzene	Perkadox 14™	169	146
Dicumylperoxide	Perkadox BC™	162	138
butyl 4,4 bis(tert butyl peroxy)valerate	Trigonox 17™	152	130
1,1 di(tert-butylperoxy)-3,3,5 trimethylcyclohexane	Trigonox 29™	138	117
tert-butyl peroxybenzoate	Trigonox C™.	136	110

Suitable peroxides can be purchased from AKZONobel (Trigonox™ or Perkadox™) or from Atofina (Luperox™) as fluids, dissolved in oil, or immobilised on silica as solid powder.

A particularly preferred peroxide is di(tertiarybutylperoxyisopropyl)benzene (available commercially as Perkadox™ 14). This peroxide has a 1 hour half life temperature of 146 °C, which makes it suitable for use at curing temperatures of from 120 to 200 °C.

Optionally, a cure accelerator can be used to increase the viscosity of the RHMA more quickly and thereby limit sagging of the extruded bead. Preferably the cure accelerator is used in an amount of from 2 to 10 %, more preferably from 4 to 6 % by weight based on the total composition. Suitable cure accelerators are diallyl terephthalate, triallylcyanurate, triallylisocyanurate, 1,2-poly butadiene, styrene–butadiene copolymers, divinylbenzene, trimethylolpropane trimethacrylate, polyethylene glycol dimethacrylate, ethylene glycol dimethacrylate, pentaerythritol triacrylate, allyl methacrylate, N, N –m-phenylene bismaleimide, toluenebismaleimide-p-quinone dioxime, nitrobenzene, diphenylguanidine. Preferred cure accelerators are triallylcyanurate (for example TAC from Lehmann & Vos & Co.), 1,2-polybutadiene (for example Ricon™ from Crayvalley), Styrene-Butadiene copolymers (for example Ameripol™ 4503 from Ameripol or Kraton™ D1161 from Kraton) and trimethylpropane trimethacrylate(for example Sartomer™ 350 from Crayvalley).

The composition of the invention also comprises a filler. The filler serves to decrease the tendency of the molten material to form threads and tails when the molten material is applied to a surface by extrusion. Certain fillers can also increase the viscosity at low shear rates by producing a thixotropic effect. The filler is employed in an amount of from 10 % to 40 %, more preferably from 15 % to 35 %, and most preferably from 25 to 35 %, by weight, based on the total composition. The filler is typically an inorganic mineral, such as calcium carbonate, magnesium silicate (talc), calcium silicate (wollastonite). The use of basic materials such as calcium carbonate, which are capable of neutralising any acids which may be present in the resin, is desirable, as such materials act as corrosion inhibitors. Suitable fillers are precipitated calcium carbonate or ground calcium carbonate from Solvay (for example Socal™ 312V), calcium carbonate from Imerys (for example Gama Sperse 80) or Omya, magnesium silicate from Talc Luzenac or Hipro Trading, and calcium silicate from Nyco. Preferred fillers are talcum HTP1c from HIPRO, calcium carbonate Gama Sperse 80 from Imerys, wollastonite Nygloss 8 from Nyco, or combinations thereof.

Additional conventional additives, such as oils (for example mineral oils), and colouring agents may also be employed. Such additional components generally constitute no more than 4% by weight, based on the total composition.

Compositions intended for use as anti-flutter sealers preferably also comprise a foaming agent, which is compatible with the other components and capable of expanding or decomposing on heating, such as when the composition is cured, in order to lower the density of the final cured material. Foaming agents are well known to those of skill in the art. Examples of suitable foaming agents are azo compounds, such as azodicarbonamide, azodiisobutyro-nitrile, barium azodicarboxylate, nitroso compounds such as N,N'-dimethyl-N,N'-dinitrosoterephthalamide, hydrazides such as benzenesulfonhydrazide, p,p-oxybis (benzenesulfonylhydrazide), carbazides, such as 4,4-oxybenzene sulfonyl semicarbazide, p-toluene sulfonyl semicarbazide, triazines such as trihydrazino triazine, and reactive couples such as mixtures of citric acid and sodium bicarbonate. Such materials may be used singly or in combinations of two or more thereof. Suitable commercially available foaming agents include products sold

under the names Hydrocerol ™ (from Boehringer Ingelheim) , Celogen™ OT, AZ, AZNP, and RA (from Crompton), Ficel™, Genitron™ and Planagen ™ (from Bayer), and Safoam™ FP, RPC and RIC FP (from Reed International Corporation). Preferred foaming agents are p,p-oxybis(benzenesulfonylhydrazide) (for example Celogen™ OT) and azodicarbonamide (for example Celogen™ AZ).

The foaming agent preferably provides an expansion of the composition of from 10 to 250 % during curing, more preferably from 80 % to 250 %, most preferably from 150 % to 250 %. Typically the foaming agent is used in an amount of from 0.1 % to 4 % by weight, based on the total composition.

Optionally a composition for use as an anti-flutter sealer can additionally comprise a cell regulator. The cell regulator is preferably employed in an amount of from 1 to 2 % by weight of the total composition. The purpose of a cell regulator is to lower the cell size and increase the expansion rate of the composition on curing. The cell regulator is preferably a mixture of barium para tertiary butyl benzoate and lauryl benzenesulfonic acid in oil. This cell regulator is commercially available for example as MARK™ K136 from Crompton – Witco vinyl additives.

In a further aspect of the invention there is provided a method of producing a pelletised composition, comprising formulating the above components, and pelletising the resulting composition.

The composition is typically produced in a thermoplastic process for example the thermoplastic process found in a compounding unit. Compounding units which may be used are single screw extruders, twin screw extruders, planetary extruders, ring extruders, batch internal mixers, kneaders or mixers such as those sold by Banbury, Farrell, Buss, or Kobe, or similar. In order to produce the compositions of the present invention, the mixing process preferably has a maximum processing temperature of less that 150°C, more preferably less than 130°C and a mixing time of less than 5 minutes, more preferably less than 2 minutes. The processing temperature and mixing time are important to ensure that the peroxide and foaming agent have not been activated during the production of the RHMA composition.

Pelletisation is generally carried out under-water, preferably using a die face cutter.

The pellets of the composition are free flowing at room temperature but to allow transport in large containers, in which temperatures can reach 40 to 50 °C, a pellet coating may be required. The pellet coating is preferably one or more of a powder coating comprising the filler (d), applied to the composition in an amount of from 0.2 to 2.0 % based on the weight of the composition, and optionally an anti-cluster additive added in the pellet water. Preferably, the pellet water additive is a siloxane oil (for example those supplied undr the trade Marks DC290 or DC200/350 from Dow Corning), an oxyalkylate (for example EC9092A™ from Nalco Exxon) or a water dispersion of polyethylene (for example Hordammer PE 03™ from Hoegst). The use of siloxane DC200 in combination with from 1 to 2 % talc results in fre-flowing pellets at temperatures of up to 45°C

In a third aspect of the invention, there is provided a method of adhering a first component to a second component, comprising the steps of melting a composition as described above, contacting the first and second components with the melted composition; and applying heat to cure the composition.

Preferably, the composition is applied to a substrate at temperatures from 90 to 120°C and is cured at a temperature of from 120 to 200°C, preferably from 140 to 180°C, more preferably from 150 to 170°C.

The composition of the present invention is preferably applied to a substrate by means of an applicator which has limited temperature and time exposure to the composition prior to the composition being applied to the substrate. Conventional RHMA equipment can be used if the temperature of application is less than 150°C, preferably less than 130°C and the time at the temperature of application is less than 10 minutes, preferably less than 3 minutes. A preferred application system uses a heated pumping screw equipped with an accumulator which feeds the RHMA directly onto the substrate.

A number of preferred embodiments of the invention are described in detail in the following Examples.

Examples 1-10 Anti-flutter RHMAs

Various reactive hot melt adhesive compositions were prepared by compounding the materials listed in Table 2 or Table 3. In each case, the materials were compounded using a BERSTORFF ZE40™ extruder equipped with a diverter and pelletised using a GALA™ under-water pelletiser. In each case the run produced 500kg of composition.

The raw materials were fed into the extruder using four dosing units and one liquid pump. The liquid pump was used to inject the diisodecylphthalate (DIDP) plasticiser. The raw materials were fed into the extruder either through the main throat of the extruder or via a side-feeding unit. The calcium carbonate filler was either added through the main throat, or via the side feeder.

The following are the conditions used for two alternative production methods:

Table 1

	Calcium Carbonate via main throat	Calcium Carbonate via side feeder
Polymer Mixture	main throat	main throat
Calcium Carbonate (SOCAL™)	main throat	side feeder
Tackifier (Hydrocarbon Resin)	main throat	main throat
Peroxide/Rubber Accelerator/ Foaming Agent/Pigment	main throat	main throat
Plasticiser (Diisodecylphthalate (DIDP))	side feeder	side feeder
Barrel Temperatures	80°C	80°C
UWG Die Plate Temp.	95°C	95°C
Adapter and Diverter Temp.	80°C	80°C
Extruder Conditions	100rpm, 40% Torque	160rpm, 43% Torque
Die pressure	77 bar	77 bar
Melt temperature	93-95°C	95°C
Output	50-60kg/hour	80kg/hour

It was found that, when the side feeder was used to add the calcium carbonate, it was possible to obtain higher throughputs. It was important to keep the feed-zone as cold as possible with cooling water to minimise powder build-up (of pigment and hydrocarbon resin tackifier) in the feed-zone.

For hot melts a minimum viscosity of 3 Pa.s is required in order to allow under water granulation. The compositions of Tables 2 and 3 meet this requirement. Constant run conditions are observed with a melt temperatures of less that 100°C and a residence time of less than one minute. The GALA™ under-water pelletiser is usually used with anti-blocking agents for hot melts. However, the compositions of Tables 2 and 3 do not require anti-blocking agents.

The above method was used to prepare the RHMA formulations shown in Table 2, which shows the amounts of each component as % by weight, based on the total composition

Table 2

Example No	1	2	3	4	5	6	7	8	9	10
Ethylene/acrylic acid copolymer (PRIMACOR 5990i™)	29.6	13.3	15.2	16.0	13.0	13.2	18.3	14.5	33.6	24
Ethylene/vinyl acetate copolymer (for example ESCORENE UL 05540™)	9.9	13.3	12.2	10.0	13.0	13.2	8.9	13.9	0.0	9.6
Divinylbenzene/butadiene copolymer rubber (AMERIPOL 4503™)	4.9	8.9	8.8	8.7	8.7	13.2	8.9	7.0	9.6	4.8
Ethylene/acrylic ester/glycidylmethacrylate copolymer (LOTADER AX 8900™)	4.9	8.9	8.8	8.7	8.7	4.4	8.9	7.0	4.8	9.6
Cyclopentadiene resin tackifier (NECIRES LF 220/100™)	13.3	13.3	13.2	13.0	13.0	13.2	13.9	13.3	12.9	12.9
Calcium carbonate(SOCAL 312™)	30.5	33.2	32.6	32.6		32.6	32.9	34.8	29.8	
Talcum(HIPRO HTP1c™)					32.6					28.8
Di(tertiarybutylperoxyisopropyl)benzene (PERKADOX 14-40 Bpd™)	2.0	1.8	1.8	1.7	1.7	1.8	1.8	1.9	1.9	1.9
diphenyl oxide 4,4 disulfonylhydrazide foaming agent (CELOGENE O.T.™)	2.0	2.0	3.1	4.1	4.1	3.1	3.1	2.1	4.6	4.6
di-isodecylphthalate(Jayflex DIDP)	2.0	4.4	4.4	4.3	4.3	4.4	3.1	4.6	1.9	1.9
Carbon black (Z 312™)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

In all cases, the compositions produced free-flowing, non-sticky granules. A smooth bead with good adhesive properties could be extruded at temperatures of from 100 to 120°C without activating the peroxide and/or foaming agent. After curing at 180°C, satisfactory expansion, excellent adhesion and softness (measured by means of shore A according to the test ISO868) were obtained. The compositions were therefore suitable for use in anti-flutter applications. The extruded beads of all of the compositions showed no sagging when heated to 180°C for 30 minutes on a 90° tilted metal sheet.

Examples 11-18 Seamsealer RHMAs

A reactive hot melt adhesive for use as a seam sealer does not require expansion and therefore does not require a foaming agent. Such adhesives were prepared using the same general method of Examples 1 to 10, using the following components:

Example No	11	12	13	14	15	16	17	18
Ethylene/acrylic acid copolymer (PRIMACOR 5990i™)			27	32.6	32.6	32.7	28	28
Ethylene/vinyl acetate copolymer (ESCORENE UL 05540™)	29.7	45.5	10.2	15.8	15.8	15.8	10	10
Divinylbenzene/butadiene copolymer rubber (AMERIPOL 4503™)	7.4		8.2					
Ethylene/acrylic ester/glycidylmethacrylate copolymer (LOTADER AX 8900™)	7.4						10	10
Cyclopentadiene resin tackifier (ESCOREZ 2101™)	14.9	15.5	15.3	13.5	13.5	13.5	14	14
Calcium carbonate(SOCAL 312™)	32.6	30.8	32.7	31.5		15.2		
Talcum(HIPRO HTP1c™)					31.5	15.2		
Wollastonite(Nyad 8)							30	
Calcium Carbonate(Gama Sperse 80)								30
Di(tertiarybutylperoxyisopropyl)benzene (PERKADOX 14-40 Bpd™)	2	2	2	2	2	2	2	2
di-isodecylphthalate (Jayflex DIDP)	5	5.2	5	3.6	3.6	3.6	5	5
Titanium dioxide	1	1	1	1	1	1	1	1

The amounts of each component used are percentages by weight, based on the total composition. Examples 11 and 12 contain no EAA and are Comparative Examples.

Examples 1 to 4 and 11 to 14 – Lap shear test

The adhesive properties of the compositions of Examples 1 to 4 and 11 to 14 were tested using DIN 53253 after oven curing at 180°C for 30 minutes and also after ageing by cataplasma corrosion test for time intervals of 7, 14 and 21 days.

Cataplasma Corrosion Test

Three samples are prepared according to the tensile lap shear strength test . A cotton wool strip of approximately 180 mm by 500 mm is cut and then weighed. It is typically of weight 45 g ± 5 g. The first sample is placed on the first third of the length of the cotton wool and covered with cotton wool. The second sample is placed on the second third of the length of the cotton wool and is also covered with cotton wool. The third sample is placed on the final third of the length of the cotton wool and covered with cotton wool. The three samples and the cotton wool are then placed in a polyethylene bag. Deionized water with a mass of two times that of the cotton wool is then added to the bag and distributed as evenly as possible over the cotton wool. As much air as possible is removed from the bag by manually flattening and smoothing the bag. The opening of the bag are sealed by melting the polyethylene using heating tongs. To ensure that the samples are well sealed within the bag, the first bag is then placed in a second bag and sealed in the same manner. The bag(s) containing the samples are placed in a chamber having a temperature of 70°C ± 2°C for 7 days. The above steps should be repeated with further samples of the same composition and the bags placed in the chamber for 14 days and 21 days. After the ageing of the samples for 7, 14 or 21 days, the samples are removed from the bags and the cotton wool and placed for two hours in a chamber having a temperature of -20°C ± 2°C. The samples are then tested using the lap shear test DIN 53253 .

Desirably, fresh and aged compositions should show cohesive failure rather than adhesive failure, and have a lap shear strength of at least than 0.5 MPa.

Table 4

	Lap Shear Strength (MPa)			
Formulation Nr.	1	2	3	4
Initial Reference (Galvanised steel)	0.57 CF	0.18 CF	0.21 CF	0.39 CF
	0.57 CF	0.17 CF	0.91 CF	0.43 CF
7 days ageing method H (Galvanised steel)	0.7 CF	0.3 AF	0.3 AF	0.5 AF/CF
14 days ageing method H (Galvanised steel)	0.8 CF	0.4 AF	0.3 AF	0.6 AF/CF
21 days ageing method H (Galvanised steel)	0.8 CF	0.3 AF	0.45 AF	0.5 AF/CF
Initial Reference Aluminium 6016	0.75 CF	0.21 CF	0.40 CF	0.33 CF
	0.73 CF	0.2 CF	0.43 CF	0.32 CF
7 days ageing method H (Aluminium 6016)	0.85 CF	0.3 AF	0.4 AF	0.7 AF/CF
14 days ageing method H (Aluminium 6016)	1.0 CF	0.45 CF	0.4 AF	0.55 AF/CF
21 days ageing method H (Aluminium 6016)	1.0 CF	0.4 AF	0.55 AF	0.6 AF/CF

The results of the lap shear test are presented in Tables 4 and 5. The results show that for anti-flutter reactive hot-melts, Examples 1 and 4, in which the most preferred amount of EAA is present in the composition, show cohesive failure after oven curing at 180°C and subsequent testing after 21 days cataplasma corrosion testing. Examples 2, 3, and 4 have a lower initial lap shear strength before and after cataplasma testing than Example 1, and also demonstrate adhesive failure in some cases. Examples 2, 3, and 4 are thus less preferred than Example 1. For seam-sealer adhesives, the results show that Example 13 and 14, in which EAA is present in the composition, show cohesive failure after oven curing at 180°C and subsequent cataplasma corrosion testing for 21 days. Comparative Examples 11 and 12, containing no EAA, have a lower initial lap shear strength before and after cataplasma testing than Example 13 and 14, and also demonstrate adhesive failure in some cases.

Table 5

Formulation Nr.	Lap Shear Strength (MPa) 11	12	13	14
Initial Reference (Galvanised steel)	0.22 AF	0.19 CF	0.86 CF	0.79 CF
	0.20 AF	0.18 CF	0.91 CF	0.83 CF
7 days ageing method H (Galvanised steel)	0.35 CF/AF	0.25AF/CF	0.96 CF	0.85 CF
14 days ageing method H (Galvanised steel)	0.40 AF	0.38AF/CF	1.10 CF	0.96 CF
21 days ageing method H (Galvanised steel)	0.41 AF	0.35AF	1.05 CF	0.85 CF
Initial Reference Aluminium 6016	0.28 AF	0.24 CF/AF	0.78 CF	0.73 CF
	0.31 CF/AF	0.23 CF	0.84 CF	0.82 CF
7 days ageing method H (Aluminium 6016)	0.35 AF	0.32 AF	0.96 CF	0.75 CF
14 days ageing method H (Aluminium 6016)	0.38 AF	0.44 CF	0.89 CF	0.85 CF
21 days ageing method H (Aluminium 6016)	0.42 CF/AF	0.40 AF	0.92 CF	0.96 CF

CF = cohesive failure

AF = adhesive failure

<u>Examples 1 to 10 - Expansion Rate test</u>

The expansion rate, density before and after curing and hardness before and after curing of the compositions of Examples 1 to 10 were measured, in order to assess the suitability of the adhesives as anti-flutter sealants. The results are shown in Table 6. The results show that expansion rates of 80 to 200% are obtained and that hardness (measured by means of the ISO868 test) decreases on curing.

Table 6

Example	Expansion Rate % (Method 1180)	Density Before Curing (Archimede) M/V	Density After curing M/V	Shore A Hardness Before Curing	Shore A Hardness After Curing
1	191	1.253	0.422	85	55
2	80	1.149	0.622	73	65
3	114	1.078	0.492	70	55
4	150	1.119	0.435	72	55
5	134	1.193	0.501	77	55
6	153	1.242	0.483	79	60
7	154	1.261	0.486	80	60
8	157	1.2691	0.486	82	63
9	174	1.237	0.444	76	55
10	173	1.257	0.451	82	58

The compositions according to the invention have very desirable pre-cure flow properties, the viscosity of the mixture decreasing markedly as the shear rate is increased. They may be pelletised, using conventional pelletising apparatus, in order to provide dry pelletised compositions, which are free-flowing at ambient temperatures, and not prone to stickiness or tackiness. They can nevertheless be applied as reactive hot melt compositions at temperatures normally employed in a manufacturing environment, and using either conventional application equipment for example melt pumps, or equipment designed for pellet processing, for example modified extruders.

The compositions of the invention are additionally able to produce a dimensionally stable polymer bead which has good adhesion with the metal substrate. At least the preferred embodiments show no sagging or bead deformation during anticorrosion treatment at 180°C for 30 minutes, have a lap shear strength of greater than 0.5 MPa DIN 53253 when the adhesive is fresh and also after ageing for 21 days using the cataplasma corrosion test described above, and are capable of inhibiting corrosion.

The preferred anti-flutter compositions have an expansion of greater than 150 % after curing for 30 minutes at 180°C

Generally the compositions of the invention do not require the use of zinc acrylate adhesion promoter, as is required by various prior art compositions.

Whilst the invention has been described with reference to the preferred embodiments, it is to be appreciated that many modifications and variations are possible within the scope of the invention.

Claims

1. A reactive hot melt composition in the form of free-flowing pellets, the composition comprising:
a cross-linkable resin including at least one copolymer of ethylene with an ethylenically unsaturated monomer, the resin including one or more of an ethylene-acrylic acid copolymer, an ethylene-methacrylic acid copolymer, and an ethylene-acrylic acid-methacrylic acid terpolymer; and
a free radical cross-linking initiator having a 1 hour half-life temperature of from 110 to 170°C.

2. A composition as claimed in claim 1, wherein the said resin constitutes from 37 to 60 % based on the total weight of the composition,

3. A composition as claimed in claim 1 or claim 2, wherein the composition also comprises from 10 to 30 % based on the total weight of the composition, of an adhesion promoter for providing adhesive properties to the composition at temperatures of from 50 to 100°C, wherein the adhesion promoter comprises at least one of a plasticiser and a tackifier.

4. A composition as claimed in any one of the preceding claims, which also comprises from 10 to 40 % based on the total weight of the composition, of a filler.

5. A reactive hot melt composition in the form of free-flowing pellets, the composition comprising:
a) from 37 to 60 % based on the total weight of the composition of a cross-linkable resin including at least one copolymer of ethylene with an ethylenically unsaturated monomer;
b) from 10 to 30 % based on the total weight of the composition of an adhesion promoter for providing adhesive properties to the composition at temperatures of from 50 to 100°C, wherein the adhesion promoter comprises at least one of a plasticiser and a tackifier;
c) from 0.5 to 3 % based on the total weight of the composition of a free radical cross-linking initiator having a 1 hour half-life temperature of from 110 to 170°C;

and

d) from 10 to 40 % based on the total weight of the composition of a filler; wherein component a) includes one or more of an ethylene-acrylic acid copolymer, an ethylene-methacrylic acid copolymer, and an ethylene-acrylic acid-methacrylic acid terpolymer.

6. A composition as claimed in claim any one of the preeding claims, wherein the one or more of ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, and ethylene-acrylic acid-methacrylic acid terpolymer is present in an amount of from 10 to 40 % based on the weight of the total composition.

7. A composition as claimed in claim 6, wherein the one or more ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, and ethylene-acrylic acid-methacrylic acid terpolymer is present in an amount of from 15 to 30 % based on the weight of the total composition.

8. A composition as claimed in any one of the preceding claims, wherein the free radical cross-linking initiator is a peroxide.

9. A composition as claimed in claim 8, wherein the peroxide is di(tertiarybutylperoxyisopropyl)benzene.

10. A composition as claimed in claim 3, or any one of claims 5 to 9, wherein the adhesion promoter comprises both a plasticiser and a tackifier.

11. A composition as claimed in claim 3, or any one of claims 5 to 10, wherein the tackifier is a hydrocarbon resin.

12. A composition as claimed in claim 3, or any one of claims 5 to 11, wherein the tackifier is a cyclopentadiene resin.

13. A composition as claimed in claim 3, or any one of claims 5 to 12, wherein the plasticiser is an alkyl phthalate.

14. A composition as claimed in any one of the preceding claims, wherein the resin comprises one or more of a terpolymer containing acrylate and/or methacrylate units, a maleic anhydride grafted elastomer, an ethylene-acrylate-glycidyl methacrylate polymer, an ethylene-acrylate-maleic anhydride polymer, an ethylene-vinyl acetate-maleic anhydride polymer, an ethylene-vinyl acetate

copolymer, an ethylene-methylacrylic ester copolymer, an ethylene-ethylacrylic ester copolymer, a ethylene-butylacrylic ester copolymer and a rubber.

15. A composition as claimed in claim 14, wherein the ethylene-vinyl acetate copolymer is present in an amount of from 5 to 20%, based on the total weight of the composition.

16. A composition as claimed in claim 14 or claim 15, wherein one or more of the methacrylate- and acrylate-containing copolymers or terpolymers is present in a total amount of up to 30 %, based on the total weight of the composition.

17. A composition as claimed in any one of claims 14 to 16, wherein one or more of the methacrylate- and acrylate-containing copolymers or terpolymers is present in an amount of from 4 to 14%, based on the weight of the total composition.

18. A composition as claimed in any one of claims 14 to 17, wherein the rubber is present in an amount of up to 30 % by weight, based on the total composition.

19. A composition as claimed in claim 18, wherein the rubber is a divinyl benzene-butadiene copolymer.

20. A composition as claimed in any one of the preceding claims, further comprising an oil.

21. A composition as claimed in any one of the preceding claims, further comprising a foaming agent in an amount of from 0 % to 4 % by weight, based on the total composition.

22. A composition as claimed in claim 21, wherein the foaming agent is one or more of azodicarbonamide, azodiisobutyro-nitrile, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, benzenesulfonhydrazide, p,p-oxybis (benzenesulfonylhydrazide), 4,4-oxybenzene sulfonyl semicarbazide, p-toluene sulfonyl semicarbazide, trihydrazino triazine, and mixtures of citric acid and sodium bicarbonate.

23. A composition as claimed in claim 21 or claim 22, wherein the composition expands by from 150 to 250 % on curing.

24. A method of preparing a pelletised reactive hot melt composition adhesive composition as claimed in any one of claims 1 to 23, comprising:

compounding the components of the composition; and

pelletising the resulting composition to produce a dry free flowing material.

25. A method as claimed in Claim 24, wherein the components are compounded at a temperature of less than 150°C.

26. A method as claimed in Claim 24 or Claim 25, wherein the components are compounded for a time of less than 5 minutes.

27. A method of adhering a first component to a second component, comprising the steps of melting a composition as claimed in any one of claims 1 to 23, contacting the first and second components with the melted composition; and applying heat to cure the composition.

Abstract

A reactive hot melt composition in the form of free-flowing pellets. The composition comprises from 37 to 60 % based on the total weight of the composition of a cross-linkable resin including at least one copolymer of ethylene with an ethylenically unsaturated monomer and wherein the cross-linkable resin includes an ethylene-acrylic acid or ethylene-methacrylic acid copolymer, from 10 to 30 % based on the total weight of the composition of an adhesion promoter, which is a plasticiser and/or a tackifier, for providing adhesive properties to the composition at temperatures of from 50 to 100°C, from 0.5 to 3 % based on the total weight of the composition of a free radical cross-linking initiator having a 1 hour half-life temperature of from 110 to 170°C and from 10 to 40 % based on the total weight of the composition of a filler.